Synthesis of an End-Capping Agent and Its Use in a Co-Block Polymerization

Developing an Undergraduate Experiment in Polymer Chemistry

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Introduction

A better understanding of polymer properties and the development of new methods to synthesize and modify them are continuing areas of basic research. Despite the impact of polymer chemistry on modern society and the fact that many graduating chemists will work in this area, there are very few polymer experiments designed for the undergraduate laboratory, and fewer still that involve recent advances in polymer synthesis. Additionally, with the new ACS undergraduate degree guidelines in effect, it is important to design an experiment that can be used in the undergraduate curriculum and allow exposure to polymer chemistry. Though the use of macroinitiators is an important method for the preparation of block copolymers with highly controllable architectures, there are currently no reported undergraduate experiments involving their preparation or application. To contribute to this area we plan to develop several advanced experiments in polymer chemistry. Particular emphasis will be placed on the combined contributions from multiple areas of chemistry (organic, physical, polymer, etc.) to the development of new polymeric materials and methodologies. Here we report our initial progress on the first such experiment which focuses on the synthesis and use of macroinitiators in the preparation of block copolymers.

Educational Objectives

Key objectives of this project are for students to learn how important interactions across the boundaries between the different disciplines in chemistry can be. Such Integrated Laboratory Experiences (ILEs) are critical to the proper training of chemists.

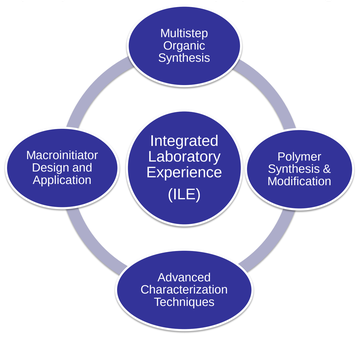
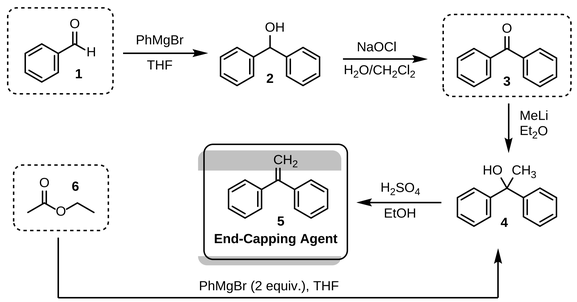


Figure 1. ILE Multidiscipline Crossover.

This experiment is appropriate for an upper level laboratory course in advanced organic or polymer chemistry. The ILE described here involves multi-step organic synthesis, product separation and purification, polymer synthesis and modification, as well as advanced characterization techniques. Additionally, students will learn how to perform chemical research through the exploration of different reaction conditions that are tested and directly compared to one another to determine the best option for synthesis.

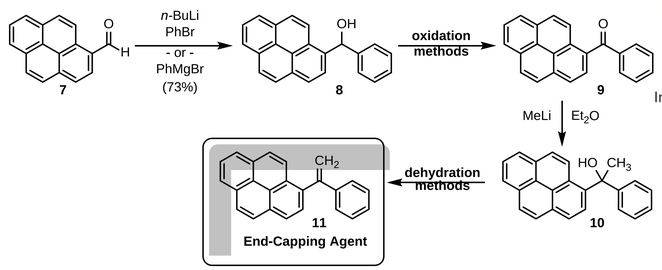
Experimental Design and Initial Results

Phase I – Multistep Organic Synthesis of End-Capping Agents



Scheme 1. Synthesis of 1,1-diphenylethylene.

In order for this experiment to be flexible for multiple institutions, one end-capping agent (**5**) can be accessed via three inexpensive compounds: benzaldehyde (**1**), benzophenone (**3**), or ethyl acetate (**6**). Depending on the chemicals on hand or time available to spend on the synthesis an instructor could choose to start the synthesis from any of these three compounds (Scheme 1). Other aromatics can also be used (e.g. compound **7**) to begin the synthesis (Scheme 2).



Scheme 2. Synthetic plan for 1-(1-phenylethenyl)-pyrene.

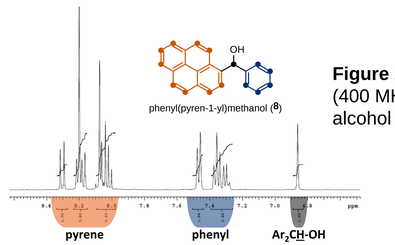
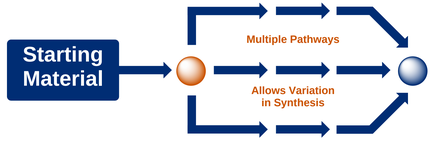


Figure 2. Important ^{1}H NMR (400 MHz, $CDCl_3$) signals of alcohol 8.

Experimental Variation Encouraging Collaborative Efforts



The experimental design also lends itself toward collaboration between students or lab groups. Work is currently underway to explore oxidation methods (e.g. other than NaOCl) that will allow for the transformation of **2** to **3** (Figure 4). Sodium hypochlorite was chosen due to its cost and availability. However, assigning other oxidation reactions would allow lab students to discuss the benefits and downfalls of specific reactions. Additional methods for transformations in the synthetic pathways will be added in an effort to make this experiment even more modular (Schemes 1 and 2).

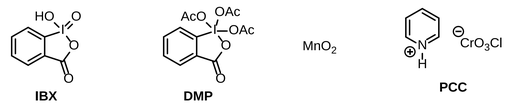


Figure 4. Potential oxidizing reagents to explore.

Phases II & III – Macroinitiator Synthesis/Block Polymerization

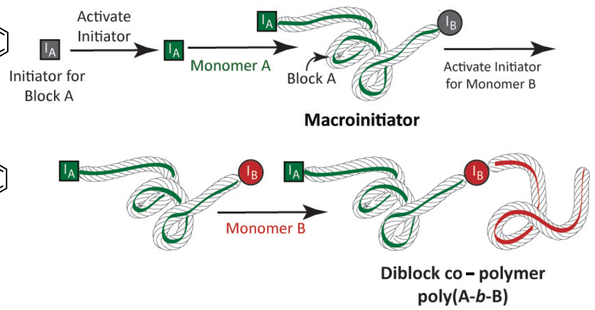


Figure 5. Use of macroinitiator in block polymerization.

Block copolymers are polymers consisting of two or more monomeric clusters with end-cap intermediate groups which connect these different monomers. Block copolymers are found in real world settings such as SBS rubber (Styrene-Butadiene-Styrene) in automobile tires and other commercial uses. Synthesis of block copolymers is important due to its potential wide-range applications made possible through manipulation of these different monomeric clusters and end-cap groups.

End-Capping Agents

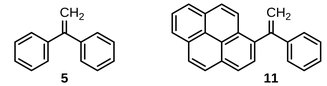
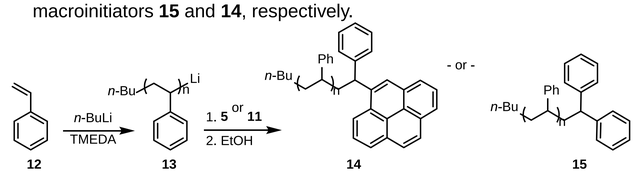


Figure 6. End-capping agents.

Both end-capping agents will be utilized, once completely synthesized, and used in the copolymerization shown below.

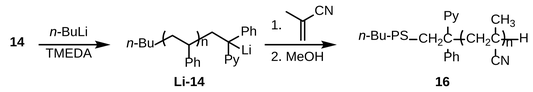
Copolymer Preparation (Phase II/III)

Phases II and III of this experiment involve the synthesis and characterization of a terminally functionalized polystyrene oligomers and their subsequent use as anionic macroinitiators in the formation of block copolymers. Initial macroinitiators will be prepared by the living anionic polymerization of styrene (Scheme 3) and subsequent terminal functionalization with **5** and **8** to form the anionic macroinitiators **15** and **14**, respectively.



Scheme 3. End-capping of polystyrene.

Macroinitiators **14** and **15** can then be activated using *n*-butyllithium in dry THF and used in the polymerization of methacrylonitrile (Scheme 4). After quenching the living end-groups with degassed CH_3OH, the block copolymer will be isolated by precipitation into excess methanol and dried in vacuo.



Scheme 4. Poly(styrene-b-methacrylonitrile) synthesis.

References

- For information regarding an earlier synthesis of **5**, see: Quirk, R. P.; Schock, L. E. *Macromolecules* **1991**, *24*, 1237–1241.
- For information related to NBS mediated conversion of 3° ROH to an alkene, see: Ajvazi, N.; Stavber, S. *Molecules* **2016**, *21*, 1325.

Acknowledgements

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